Influence of Pressure on Smectic A-Nematic Phase Transition

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Abstract

We propose a Landau-de Gennes phenomenological model to describe the pressure induced smectic A-nematic phase transition. The pressure induced smectic A phase transitions are discussed for varying coupling between orientational and translational order parameter. Increasing the pressure, the first order nematic-smectic A transition becomes second order at a tricritical point which agrees fairly with available experimental results.

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1 Introduction

In spite of considerable research activity over the past twenty years the nematic to smectic A (NA) phase transition remains one of the principal unsolved problems in equilibrium statistical physics. During the past twenty years, many high resolution heat capacity and x-ray studies have been devoted to the NA transition [1-11]. The theory of the NA transition has also received considerable attention [12-20]. At the NA phase transition the continuous translational symmetry of the nematic phase is sponteneously broken by the appearence of one dimensional density wave in the smectic A phase. Original theories due to McMillan [13] and de Gennes [14] suggested that NA transition could be first or second order. The order of the transition changes at a tricritical point (TCP). Alben [21] predicted a ^{3}He-^{4}He-like TCP in binary liquid-crystal mixtures. However, Halperin, Lubensky and Ma [15] argued that NA transition can never be truly second order, which ofcourse rules out the possibility of a TCP. This controversy has spurred experimental studies [1-11] which have shown that NA transition can indeed be continuous when measured to the dimensionless temperature $(T - T_{NA})/T_{NA} \approx 10^{-5}$. Also, the Landau and molecular field theories for the tricritical point are discusses by Longa [22]. In a very recent paper [19] Lelidis and Durand predicted the field induced TCP in NA transition.

Again a pressure induced TCP of NA transition was studied experimentally by Mckee et al. [23]. They examined the effects of pressure on the NA transition by measuring a quantity proportional to the nematic order parameter, a splitting ΔH in the proton dipolar NMR spectrum, at pressure up to 3.5 kbar. They pointed out that the confirmation of a NA TCP at elevated pressure would suggest the existence of compounds with a second order transition. Again, Keyes, Weston and Daniels [24] measured turbidity on Cholesteryl oleyl carbonate, reported evidence of a change in the nature of the cholesteric-smectic A phase transition under pressure suggestive of a TCP.

The purpose of the present paper is to examine the effects of pressure on NA transion within Landau-de Gennes phenomenological theory. In this analysis we find a pressure induced TCP on NA transition as suggested by [23].

2 Model

We start by defining an order parameter for the smectic A phase. The order parameter, ψ, is defined as the amplitude of a one dimensional density wave whose wave vector, q_0, is parallel to the director (the Z-axis) :

$$\rho(\vec{r}) = \rho_0\{1 + \text{Re}[\psi e^{iq_0 z}]\}, \tag{1}$$

where $a = 2\pi/q_0$ is the layer spacing and $\psi(\vec{r}) = |\psi|e^{iq_0 u}$. Here u is the displacement of the layers in the Z-direction away from their equilibrium position (k=k(x,y,z)). We imagine that there exists a pressure which decreases the free energy density F. Hence the free energy density of the NA transition in the presence of pressure written as

$$F = F_N(T,Q) + F_A(T,\psi) + F_{AN}(Q,\psi) + F_P(Q,\psi,P), \tag{2}$$

where $F_N(T,Q)$ is the free energy density of the nematic phase, $F_A(T,\psi)$ corresponds to the smectic A phase, F_{AN} is the contribution from the coupling between Q and ψ and $F_P(Q,\psi,P)$ is the free energy density associated with the coupling of the pressure with the order parameters. Now F can be expanded in powers of nematic order parameter Q and smA order parameter ψ :

$$F_N = F_0 + \frac{1}{2}AQ^2 + \frac{1}{3}BQ^3 + \frac{1}{4}CQ^4, \tag{3a}$$

where, $A = a(T - T_{NI}^*)$, F_0 is the free energy density of the isotropic phase and T_{NI}^* is the isotropic supercooling temperature. a, B and C are independent of temperature. Because of the first order nematic-isotropic (NI) transition, $a¿0$, $B¡0$, and $C¿0$.

$$F_A = \frac{1}{2}\alpha|\psi|^2 + \frac{1}{4}\beta|\psi|^4, \tag{3b}$$

where $\alpha = \alpha_0(T - T_{AN}^*)$, T_{AN}^* is the supercooling temperature limit of the nematic phase for F_{AN}=0 and P=0. α_0 and β are constants. In the absence of coupling equation (3b) describes a second order transition. Since smectic phase cannot occur without orientational ordering, hence to ensure the smA phase F_{AN} is included in expression (2). At lowest order coupling term $F_{AN}(Q,\psi)$ can be written as follows :

$$F_{AN} = \gamma Q|\psi|^2 + \frac{\eta}{2}Q^2|\psi|^2, \tag{3c}$$

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γ and η are coupling constants. γ is chosen negetive to favour smA phase when the nematic phase exists and we choose $\eta¿0$. Generally this term allows reentrant effects [25-27]. Because of (Q,ψ) coupling the NA phase transition can be of second order or first order [14].

We discuss now the effect of pressure on NA transition. This leads to describe the coupling of the order parameters with external pressure. From symmetry consideration, the lowest order term $F_P(Q, \psi, P)$ can be written as

$$F_P = \lambda P^2 Q. \tag{3d}$$

Minimization of (2)corresponds to the equations :

$$F'_Q = \frac{\partial F}{\partial Q} = AQ + BQ^2 + CQ^3 + \gamma|\psi|^2 + \lambda P^2 + \eta|\psi|^2 Q = 0, \tag{4a}$$

$$\frac{\partial F}{\partial|\psi|} = (\alpha + \beta|\psi|^2 + 2\gamma Q + \eta Q^2)|\psi| = 0. \tag{4b}$$

The stability conditions are

$$F''_Q = \frac{\partial^2 F}{\partial Q^2} = A + 2BQ + 3CQ^2 + \eta|\psi|^2 > 0, \tag{5a}$$

$$\frac{\partial^2 F}{\partial|\psi^2|} = \alpha + 3\beta|\psi|^2 + 2\gamma Q + \eta Q^2 > 0. \tag{5b}$$

Now in addition to the high symmetry phase (isotropic phase) denoted as I one finds two other possible stable phases corresponding to (in the absence of pressure)

II) Q $\neq$ 0, $|\psi| = 0$ nematic phase ,

III) Q $\neq$ 0, $|\psi| \neq 0$ smectic phase.

Now from equation (4b) we find

$$|\psi|^2 = \begin{cases} \frac{-(\alpha + 2\gamma Q + \eta Q^2)}{\beta} & \text{if } \alpha + 2\gamma Q + \eta Q^2 < 0 \\ 0 & \text{if } \alpha + 2\gamma Q + \eta Q^2 > 0 \end{cases} \tag{6}$$

Then the equation

$$\alpha + 2\gamma Q + \eta Q^2 = 0 \tag{7}$$

indicate the existence of sm A phase. It is also clear from equation (7) that the transition to the sm A phase depends on the temperature T^*_{AN} and on the ratio γ/α_0.

Let us now recall the properties of NI transition. Since the nematic phase has only orientational order, equation (4a) simplifies to

$$F'_Q = AQ + BQ^2 + CQ^3 + \lambda P^2 = 0 \tag{8a}$$

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and the stability condition (5a) gives :

$$F''_Q = A + 2BQ + 3CQ^2 > 0. \tag{8b}$$

Inside this stability region the system is completely unstable. Equation (8a) describes the first order NI transition at the temperature T_{NI} in the absence of pressure. In the presence of pressure the NI transition becomes second order at the isolated critical point in the temperature-pressure diagram. When pressure acts on the NI transition, the minimum corresponding to isotropic state is no more $Q=0$. It is shifted to a small but non-zero value, proportional to P^2. Then at the isolated critical point NI transition becomes second order. The existence of this isolated critical point was verified by several authors [28-31]. The coordinates of the isolated critical point are

$$\begin{aligned}
Q_c &= -\frac{B}{3C}, \\
P_c^2 &= \frac{B^3}{27\lambda C^2}, \\
T_c &= T_{NI}^* + \frac{\beta^2}{3aC}.
\end{aligned} \tag{9}$$

Now to find out the variation of the pressure in the sm A phase let us now recall the solution $Q \neq 0$, $|\psi| \neq 0$. For $|\psi| \neq 0$, F can be written as function of Q alone. By substituting $|\psi(Q)|^2$ from equation (6) into equation (2) we obtain :

$$F = F_0 - \frac{\alpha^2}{4\beta} + (\lambda P^2 - \frac{\gamma\alpha}{\beta})Q + \frac{1}{2}A^*Q^2 + \frac{1}{3}B^*Q^3 + \frac{1}{4}C^*Q^4, \tag{10}$$

where the renormalized coefficients are :

$$A^* = A - (2\gamma^2 + \eta\alpha)/\beta, \tag{11a}$$

$$B^* = B - 3\eta\gamma/\beta, \tag{11b}$$

$$C^* = C - \eta^2/\beta. \tag{11c}$$

The equilibrium condition of equation (10) can be written as

$$(\lambda P^2 - \frac{\gamma\alpha}{\beta}) + A^*Q + B^*Q^2 + C^*Q^3 = 0. \tag{12}$$

Here we assume that $C > \eta^2/\beta$. When $C ¡ \eta^2\beta$ then a higher order term should be included. Let us now assume Q_{NA} be the nematic order parameter at the NA transition and $F_N(Q_{NA})$ is the free energy of the nematic phase at the NA phase transition point

and $F''_{Q_{NA}}$ is the second derivative of $F_N(Q_{NA})$ at NA point. Then the free energy F of the smectic phase can be written as,

$$F \approx F_N(Q_{NA}) + \frac{1}{2}F''_{Q_{NA}}(Q - Q_{NA})^2 + \lambda P^2 Q + \frac{1}{2}\alpha|\psi|^2 + \frac{1}{4}\beta|\psi|^4 + \gamma Q|\psi|^2. \tag{13}$$

Minimization of (13) gives

$$F''_{Q_{NA}}(Q - Q_{NA}) + \lambda P^2 + \gamma|\psi|^2 = 0. \tag{14}$$

Hence from equation (14)

$$Q = -\frac{(\lambda P^2 + \gamma|\psi|^2)}{F^*_{Q_{NA}}} + \frac{Q_{NA}}{F''_{Q_{NA}}}. \tag{15}$$

Substitution of equation (15) in equation (13) gives

$$F \approx F_N(Q_{NA}, P) + \frac{1}{2}\alpha^*|\psi|^2 + \frac{1}{4}\beta^*|\psi|^4. \tag{16}$$

Here,

$$\alpha^* = \alpha - \frac{2\gamma\lambda P^2}{F''_{Q_{NA}}} + 2\gamma Q_{NA}, \tag{17a}$$

$$\beta^* = \beta - \frac{2\gamma^2}{F''_{Q_{NA}}}. \tag{17b}$$

Hence the renormalization of the transition temperature due to the (Q, ψ^2) coupling and the pressure effect can be written as

$$\tilde{T}^*_{NA} = T^*_{NA} + \frac{2\gamma\lambda P^2}{F''_{Q_{NA}}} + 2\gamma Q_{NA}. \tag{18}$$

From equation (17b) we see that for the strong enough coupling β^* can become negative i.e. the NA transition becomes first order. To ensure stability a positive stabilizing sixth order term should be added in the free energy expansion (16). For the weak coupling, β^* remains positive and the transition becomes second order. When (Q, ψ) coupling is vanishingly weak the only influence of the pressure on the smectic order comes from the coupling between smectic order parameters and pressure. Thus the free energy (13) approximated as

$$F \approx F_N(Q_{NA}) + \frac{1}{2}F''_{Q_{NA}}(Q - Q_{NA})^2 + \lambda P^2 Q + \frac{1}{2}\alpha|\psi|^2 + \frac{1}{4}\beta|\psi|^4 + \frac{1}{2}\delta P^2|\psi|^2. \tag{19}$$

After minimization and eliminating Q, T^*_{AN} is renormalized to

$$T_{AN}(\gamma = 0) = T^*_{AN} - \frac{\delta}{\alpha_0}P^2. \tag{20}$$

In the absence of coupling, as $\delta/\alpha_0 < 0$, the (ψ, P) coupling increases the transition temperature proportional to the square of the pressure, but it does not influence the order of the transition and the two transitions in Q and ψ have been chosen stable. Now one calculates the pressure induced NA transition temperature $T_{AN}(P)$ and the order $Q_{AN}(P)$ at the transition point numerically from equations (7) and (8a). To do this calculation we have to calculate the value of coefficients. Since these value are still unknown, we are not in a position to calculate $T_{AN}(P)$ and $Q_{AN}(P)$ numerically. One concludes that $T_{AN}(P)$ is increasing with the pressure as expected. As the nematic order Q_{NA} at the transition increases with the field : $Q_{NA} \rightarrow Q_{NA} - \frac{\lambda P^2}{F''_{Q_{NA}}}$ the appearence of the smectic order at the transition has smaller influence on the nematic order.

In the absence of pressure, the NA transition at t_{AN} ($= T_{NA} - T^*_{NI}$) is of first order and shows a jump of Q because because positional order appears discontinuously. The transition temperature $T_{AN}(P)$ is defined from the conditions

$$F(Q \neq 0, |\psi| \neq 0) = (Q \neq 0, |\psi| = 0).$$

The intersection of the smectic spinodal with the equilibrium line $Q(T, P = 0)$ gives the superheating limit T^{**}_{AN} of the first order NA transition in absence of pressure. The intersection of the spinodal with the smectic line defines the TCP where the transition becomes second order with coordinates (Q_{tcp}, T_{tcp}) given by,

$$Q_{tcp} = -\frac{(B^* - a^*\gamma/\alpha_0)}{(3C^* - a^*\eta/\alpha_0)} + \sqrt{\left(\frac{B^* - a^*\gamma/\alpha_0}{3C^* - a^*\eta/\alpha_0}\right)^2 - \frac{a^*(T^*_{AN} - T^*)}{3C^* - a^*\eta/\alpha_0}}, \qquad (21a)$$

$$T_{tcp} = T^*_{AN} - Q_{tcp}(2\gamma + \eta Q_{tcp})/\alpha_0. \qquad (21b)$$

where

$$a^* = a_0 - \frac{\eta\alpha_0}{\beta}, \qquad (21c)$$

and

$$T^* = \left(\frac{a_0 T^*_{NI}}{a^*}\right) + \left(2\gamma^2 - \frac{\eta\alpha_0 T^*_{AN}}{\beta a^*}\right). \qquad (21d)$$

Thus the tricritical point is (T_{tcp}, Q_{tcp}). The "tricritical pressure" to attain the TCP is given by

$$P^2_{tcp} = \frac{1}{\lambda}\left[\frac{\alpha T_{tcp}\gamma}{\beta} - \alpha^* T_{tcp} Q_{tcp} - B^* Q^2_{tcp} - C^* Q^3_{tcp}\right]. \qquad (22)$$

Thus for $P = P_{tcp}$ the TCP appears and the transition becomes second order. Thus we point out that the confirmation of a nematic-smectic A TCP at elevated pressure would

suggest the existence of second order transition which support the experimental evidences [23].

Again from equation (21d) we find that

$$\frac{dT_{AN}^*}{dP} = \frac{a_0 \beta}{\eta \alpha_0} \frac{dT_{NI}^*}{dP},\tag{23}$$

we get

$$\frac{dT_{NI}^*}{dP} < \frac{dT_{AN}^*}{dP}.\tag{24}$$

Equation (24) agrees with the experimental observation [23].

3 Conclusion

We have developed a phenomenological model in the Landau-de Gennes formalism to describe the pressure induced phase transitions between isotropic, nematic and smectic A. The effect of pressure on the second order NA transition is to increase the transition temperature as square of the pressure. In presence of pressure, the first order NA transition (when pressure reduced to zero) becomes of second order above at TCP. The coordinates TCP have been calculated. The value of the pressure at TCP have also been calculated. Thus the present model analyze the experimental results [23].

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